

MATERIAL OUTGASSING, IDENTIFICATION and DEPOSITION, MOLIDEP SYSTEM

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Biographies

John Scialdone

Dr John Scialdone is a part-time employee of Swales Aerospace and a long time member of the IEST. He retired recently after thirty-eight years of service from NASA Goddard Space Flight Center where he had been section head, group leader and staff engineer-scientist of the Material Engineering Branch. His expertise is in spacecraft molecular and particulate contamination generated by material outgassing, on the effect of the environment on space systems, and on gas dynamics and space lubrication. His many awards include the NASA Medal for Exceptional Service, Astronauts Silver Snoopy award, the IEST Space Simulation award. He is a Fellow of the IEST. He has degrees in mechanical and aerospace engineering from the Carnegie-Mellon University, the University of Pittsburgh and the University of Naples (Italy).

Alex Montoya

Alex Montoya is an employee in the Materials Engineering Branch at NASA-Goddard Space Flight Center located in Greenbelt, Maryland. He has been in this Branch for 11 years and along with the MOLIDEP system currently works with infrared spectroscopy and thermal analysis techniques. He has a Bachelors of Science degree in Chemistry from the University of Maryland.

Abstract

The outgassing tests are performed employing a modified vacuum operated Cahn analytical microbalance, identified as the MOLIDEP system. The test measures under high vacuum, the time varying Molecular mass loss of a material sample held at a chosen temperature; it identifies the outgassing molecular components using an inline SRS 300 amu RGA and employs a temperature controlled 10 MHz QCM to measure the condensable DEposits. Both the QCM and the RGA intercept within the conductive passage the outgassing products being evacuated by a turbomolecular pump. The continuous measurements of the mass loss, the rate of loss, the sample temperature, the rate of temperature change, the QCM temperature and the QCM recorded condensable deposits or rate of deposits are saved to an Excel spreadsheet. A separate computer controls the RGA.

Keywords

Outgassing Measurements, Vacuum Microbalance, Quartz Crystal Microbalance (QCM)

Introduction

A vacuum operated analytical microbalance including an RGA and a QCM measures the mass loss and the outgassing rate of a material sample held at desired temperature. It identifies the material chemical components and measures their deposits on surfaces at various temperatures. This paper describes the facility, the operation of the individual components and describes the results of the test of a sample material.

Facility Description

The MOLIDEP Facility is shown in Figure 1. The microbalance (Figure 2) is shown between the two instrument cabinets. It consists of a 5.537cm diameter, (50cm) long cylindrical glass tube sealed at one of the bases. A cylindrical resistance heater that can be positioned at any location along or below the tube is seen surrounding the tube. The heater imparts heat to the material sample that is held in a glass basket suspended by a platinum wire. The wire is attached to the electronic mass

weighing mechanism located inside the hemispherical container shown on top of the instrument. A tare balance is also attached to the weighing mechanism. The supporting structure consists of a machine casting with a large port leading to the vacuum pumping system. The 1000 l/s turbomolecular pump and accessories are located inside the cabinet with the control knobs, pressure and temperature reading gages. The casting provides 4 access passages two of which have been utilized for the inclusion of the RGA and of the QCM and one is used for the thermocouple indicating the sample temperature. The 10MHz QCM within the cooling container intercepts an effective one cm^2 of the 44.67 cm^2 of the outgassing flow going to the vacuum port. The outgassing flow originates about 36.83 cm away at the material sample. It is completely directed by the glass tube to the vacuum pump. The RGA ionizer head is located a few cm above the QCM and near the pumping port. The coolant flow lines, the wiring and the 300 m/e RGA head are in the back of the mounting casting and are not visible in the figure. The QCM controller, the sample temperature monitoring and setting are located in the cabinet to the left of the Cahn balance. The cabinet includes also the ion and thermal vacuum gauges. The RGA controller and monitor are seen on the right of the Cahn balance.

Cahn Microbalance

Mass Loss versus Time (mg vs. hrs)

The test data provide the mass loss Δm (mg) as a function of time t (hrs) and temperature T ($^{\circ}\text{C}$) under a vacuum of about $E-7$ torr of a sample of initial mass m_0 and surface area A (cm^2): $\Delta m(T, t, E, m_0, A)$. The chosen test temperature can be from room temperature to about 125°C . The sample mass can be from milligrams to about 10 g. The reading accuracy is to 1/100 mg. The sample dimensions may have a max diameter of about 4 cm in diameter and a varying thickness. The mass loss per unit area $\Delta m/A$ (g/cm^2) or mass per unit mass (g/g) data and their graphical representations reflect the kinetics of the outgassing. The equation representing the loss can indicate: a linear loss with time (as for evaporation), an exponential junction of time (as for a first order reaction), a polynomial function (as for an high order reaction) or a square root function of time (as for a diffusion process). The time derivative of the mass loss per unit area versus time ($\text{g}/\text{hr}/\text{cm}^2$) provides the outgassing rate per unit area versus time utilizable for modeling. Repeating the mass loss test of the same material at about 3 different temperatures provides the data to evaluate the outgassing activation energy, E (cal/mole) and the effect of temperature on the outgassing rates. The mass loss data can be used to obtain the percentage mass loss of the material (TML) at any temperature and for any length of time in vacuum.

Mass Loss Rate versus Time (mg/hr vs. hrs)

The rate of mass loss with time is plotted as the outgassing test proceeds. It shows the time varying rate of outgassing $m=\Delta m/\Delta t$ (t) or g/hr and $\text{g}/\text{hr}/\text{cm}^2$. These data are needed for modeling or for calculations to estimate the pressure, the density and the contamination resulting from the material outgassing.

Temperature versus Time ($^{\circ}\text{C}$ vs. hrs)

The assigned temperature of the sample is monitored constantly during the test and can be changed if desired. The temperature is measured with thermocouples located near the sample. It is manually set and not programmable at this time.

Temperature Rate of Change ($^{\circ}\text{C}/\text{hrs}$ vs. hrs)

The data and its plot reflect the rate of change of the temperature rate as it occurs. The change may result from input temperature changes or from unwanted external effects.

Quartz Crystal Microbalance (QCM)

The identification of the sample, its dimensions and the initial mass are indicated. The desired data logging time, the QCM set temperature and the set rates of temperature change are also listed. The desired QCM temperature is obtained by utilizing the heat generated by the electrical heater available in the QCM and with the flow of liquid nitrogen circulating in the specially designed QCM container. The obtainable temperatures vary from 90°K to about 350°K . The rate of temperature change can also be set. The data obtained from the QCM are reported digitally and graphically. A single plot reports the QCM temperature T ($^{\circ}\text{K}$), the crystal frequency (Hz) and the rate of frequency change with time (Hz/time). All plotted continuously versus a preferred unit of time. The data can be presented directly in terms of material accumulation on the

crystal as g/cm^2 or rate of accumulation as $\text{g/cm}^2/\text{hr}$. These are obtained utilizing the sensitivity constant, $4.42 \times 10^{-9} \text{ g/cm}^2 \cdot \text{Hz}$ of the 10MHz QCM that is available in the software.

The total amount of condensable fraction of the outgassing sample is available by multiplying the amount per squared cm (g/cm^2), indicated by the QCM by the Cahn microbalance outgassing flow area, 44.67 cm^2 within which the QCM is immersed.

A "VCM" of the material at QCM temperature can be obtained from the above calculated total amount and the sample initial mass. This value would be a function of the condensing temperature, the sample temperature and the length of time during which collection of condensate occurred.

Condensable amounts and rates can be obtained during the test by varying the QCM temperatures also for brief lengths of time. Taking condensing rates at different temperatures for brief periods of time and sequentially during the test can provide data for the plotting of the condensation at several temperatures.

The QCM will indicate the rate of condensate released at specific QCM crystal temperatures. By a process of continuous warming of the crystal one may identify with reference to its temperatures the chemical nature of the condensate being released. This process provides a spectrum of the released material components that relates to their vapor pressures and to their identification. The total pressure in the system and the partial pressures of the released gases can be monitored by an RGA. This process may be carried out in the reverse direction i.e. with the QCM getting colder. Noting the QCM temperatures at which the deposit occurs and the monitored or suspected value of the partial (saturated) vapor pressure of the outgassing component, one may identify the depositing component.

Residual Gas Analyzer (RGA)

The gas ionizer of the RGA is located slightly above the pumping port. It intercepts the same stream of outgassing of that of the QCM. The installed RGA can scan 300 m/e.

Example of a MOLIDEP Test

An example of the utility of the MOLIDEP material testing is shown in Figure 3. The plots show the on-line recorded graphical results of the test. The test provides the change of the sample mass with time, the rate of mass loss and the temperature of the material. The mass loss deposited on the crystal of the QCM held at various temperatures is also shown graphically. The material sample is the translucent Epoxy 3M 2216 which is used for low temperature applications. The dimensions and the initial mass of the sample as measured with the Mettler microbalance are indicated. The following are some of the preliminary characterizations of the material that can be derived from the plotted data: the TML, CVCM, the equations describing the mass loss, the rate of mass loss and the deposit and removal of outgassed products from surfaces at different temperatures.

The mass loss at 40°C after 40 hrs at a pressure of about $E-7$ torr is shown from the plot to be about $6.8E-3 \text{ g}$. This value and the initial sample mass of 0.67759 g indicate that the TML is approximately 1%.

The CVCM can be obtained from the deposits on the QCM after a period of time. For 24 hrs with the QCM at -20°C , the deposit corresponds to about $(7300-7000) = 300 \text{ Hz}$. From this, the QCM sensitivity and the fact that the QCM is located within a molecular flux of 47.59 cm^2 , the CVCM for those conditions can be estimated to be $(3E2 \times 4.42E-9 \times 47.59) / 0.67759 = 9.3E-3 \%$.

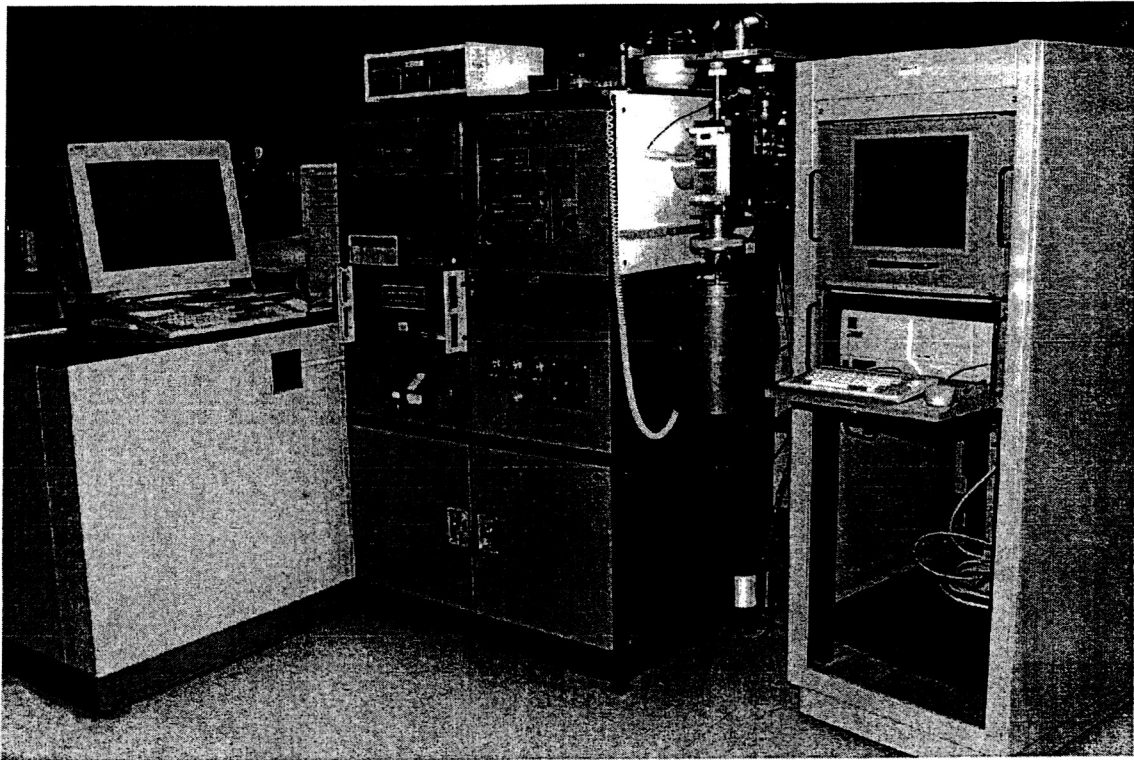
The data plot can provide an indication of the equation representing the mass loss vs. time. In this case, with the asymptotic mass loss of 8.8 mg and a time constant of about 19 hrs, the mass loss can be represented as $m = 8.8 (1 - e^{-t/19}) \text{ mg}$. The more precise equation can be obtained later from the stored numerical data using the Excel program. The mass loss can be related to the area or to the initial mass to give it mg/cm^2 or mg/g .

One of the plots of Fig.3 shows the mass loss rate (mg/hr) that is normally called the outgassing rate versus time. The equation for it can be obtained directly by differentiation of the mass loss equation. It would be for this case, $\Delta m / \Delta t = (8.8/19) e^{-t/19} \text{ mg/hr}$. Again this can be referred to the sample area or sample mass.

The QCM graphical plot of temperature ($^{\circ}\text{C}$) and frequency (Hz) vs. time shows the outgassing from the sample deposited on the QCM surface at temperatures of -20 , -40 , -60 , -50 , and -10°C . The QCM was held at -20° for about 27 hrs and the QCM showed a frequency increase of about 300 Hz. The frequency increased by about 100 Hz during the 7 additional hours at -40°C . The subsequent drop of temperature at -60°C for 13 hrs increased the frequency by 200 Hz. The temperature change to -50° for 5 hrs added 100 Hz. The slope of the deposits curve is not clearly defined during the 5 hrs. It should have a smaller slope than that at -60°C . The next temperature at -10°C released about 70 Hz in 20 hrs. The final increase of the QCM to $+45^{\circ}\text{C}$ removed most of the accumulated deposit in a very brief length of time. An analysis of the above arbitrarily programmed temperature changes of the QCM, could still provide an indication of the accumulation and the removal of the outgassing from surfaces at different temperatures. One may speculate here that connecting the largest accumulation (Hz) values for each temperature to the initial base Hz value, the accumulation vs. time at that temperature could be guessed. It would be necessary to assume that the graph from the origin to the known Hz value followed an analytical shape similar to the initially recorded at -20°C for this test. For the deposit removal, a similar approach could be used.

The RGA readings of the sample outgassing components taken during the test are shown in Figure 4. The top of the figure shows the spectrum of the material collected on the QCM at -20°C while the sample was at 40°C . It shows that the major component was H_2O with a partial pressure of about $5\text{E}-8$ torr. The total pressure was about $1\text{E}-7$ torr with the addition of the N_2 , CO , CO_2 partial pressures. The m/e peaks from 42 to 82 had partial pressures in the lower $\text{E}-10$ torr and those beyond had pressures lower than $\text{E}-10$ torr. The partial pressures after 70 hours of the sample at 40°C as collected on the QCM at -10°C are shown in the lower plot. The total pressure was then in the lower $\text{E}-8$ torr with the water peak being greater than those of the N_2 and CO_2 . The m/e greater than 44 are not shown because they have partial pressures less than $\text{E}-10$ torr.

Rev. 11/19/02



Test Facility - Molidep (Cahn/QCM/M/S System)

Figure 1: MOLIDEP Test Facility at Goddard Space Flight Center

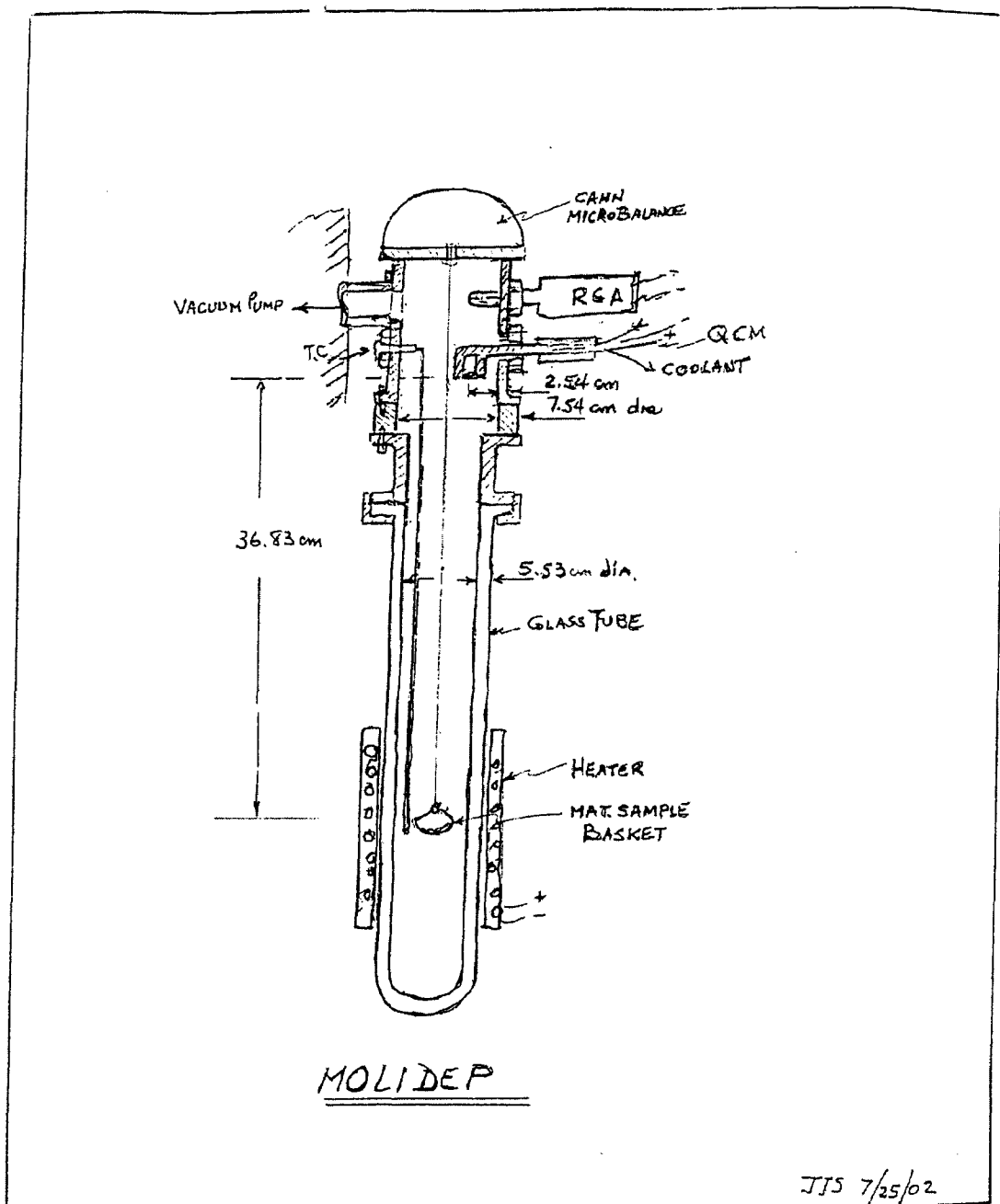


Figure 2: Sketch of the Microbalance including the QCM and the RGA

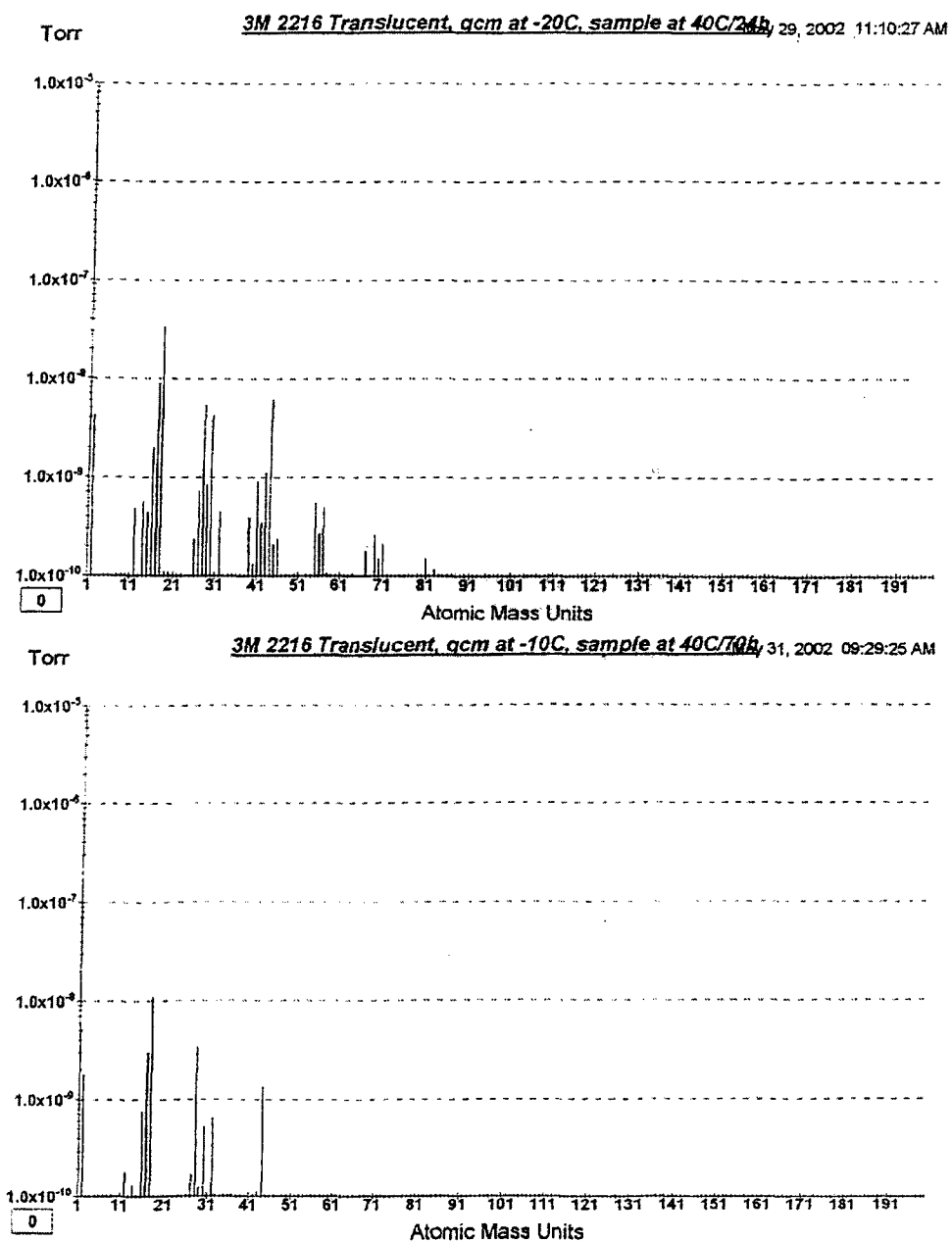


Figure 4: RGA Data Collected During Structural Adhesive Test